



Investigating the use of porous, hollow glass microspheres in positive lead acid battery plates



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H I G H L I G H T S

- Additives of porous, hollow, glass microsphere (PHGMs) are tested in battery paste.
- A simple, heuristic equation for predicting the porosity of PHGM plates is derived.
- The equation results for predicting plate porosity compares favorably with data.
- Cell discharge test results are compared with model predictions.

A R T I C L E I N F O

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Porous, hollow, glass microspheres (PHGMs) can be used to increase porosity in lead acid battery electrodes to improve the battery's power and energy performance at higher discharge rates. As reported in this paper, the PHGM additives did improve electrolyte storage and porosity in the electrodes. However, the nonconductive PHGMs do reduce the critical volume fraction (CVF) of the electrodes as predicted from conductivity models. The increase in electrode performance due to increased porosity may therefore be partially offset by the drop in capacity due to a lower critical volume fraction. Empirical equations are developed that relate the CVF and porosity of an electrode to the amount, size, and porosity of the additives in that electrode. The porosity estimates made from the empirical equations compare favorably with the experimental data from plates fabricated with these additives. The performance of electrodes with additives is estimated from computer models using the electrode's CVF and porosity as provided by the equations. Tests were performed on plates having volume loadings of PHGMs from 11% to 44% of total solids in positive electrodes to determine their effect on active material utilizations. The results from these discharge tests are reported and compared with theoretical models.

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1. Introduction

Lead acid batteries have been around for over a century and have greatly influenced our everyday lives. These batteries have high power density, low cost, are highly reversible, and nearly 100% recyclable. However, compared to other batteries such as lithium ion or nickel metal hydride, lead acid batteries have a low specific energy (Watt-hours per kilogram) [1]. This one negative attribute limits their application in situations where weight and space are a concern such as in electric vehicles (EVs) and hybrid electric

vehicles (HEVs). Despite their low specific energy, there is precedence for using these low cost batteries for vehicle use. The first successful production electric vehicle, the EV-1, was developed by General Motors from technology demonstrated in the Impact vehicle that used conventional sealed lead acid batteries to provide a cost effective range of 100 miles (160.9 km) at 55 mph (88.51 km h⁻¹).

Present production vehicles, such as plug-in hybrid electric vehicles (PHEVs), require extended electric drive operation similar to the EV-1 and would benefit from higher specific energy density batteries at the higher discharge rates. For example, a PHEV having a 50 mile (80.5 km) electric vehicle range would need a battery half the size of the EV-1 battery but with the same or better specific energy density at twice the discharge rate. Lead acid batteries need

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to be developed specifically for these new vehicles. The paste additive addressed in this paper is only one of many design innovations [2,3] being researched for new high performance lead acid batteries.

Berndt [4] predicts the theoretical capacity of lead acid batteries as 166 Wh kg^{-1} . In practice, the specific energy performance of these batteries at the one hour rate is about 30 Wh kg^{-1} . The main reason for this lack of performance is that even at low rates only about 60% of the theoretical active material of the negative plate and 50% in the positive plate react [4]. These reduced values, when compared to Berndt's theoretical specific energy, are mainly due to a large amount of un-reacted active material that contributes to the weight but supplies no energy for the battery. This phenomenon occurs because as the active material discharges and is no longer conductive, sections of active material become electronically isolated and can no longer be discharged, causing it to become dead weight [5,6]. The critical volume fraction (CVF) is the ratio of the maximum amount of active material that can be discharged to the total amount of active material in a plate. The CVF occurs when all the active material of an electrode has either reacted or been isolated by the non-conductive lead sulfate product.

Many studies have been done on the use of various additives to help counteract the low energy density problem. Nonconductive and conductive additives have both been investigated to either decrease the dead weight or increase the conductive network of the electrodes. Edwards and co-workers [7–9] specifically studied the effects of nonconductive, hollow glass microspheres (HGMs) of various sizes with the goal of replacing the dead weight of the unused active material with lightweight structural material to try to improve active material utilization. Processes have been developed to make porous hollow glass microspheres (PHGMs) which when used in plates should further improve their specific energy performance through increased electrolyte storage and improved diffusion. The Savannah River National Laboratory (SRNL) has developed methods to produce PHGMs [10–12], and the University of Idaho also developed a method for producing these additives [13,14] as shown in Fig. 1. Methods have also been reported for

producing hollow nanoparticles [15] and porous, hollow micro-size spheres [16].

Conductive additives used in electrodes have been found to improve formation, utilization, and life of the lead acid battery [17–20]. Conductive additives such as carbon black, carbon fibers, tin oxide, and tin dioxide have all been tried with variable results [17–19]. Titanium fibers have been previously tested and successfully used to increase the utilization in the positive plate to approximately 64% [20]. Further research has demonstrated processes to create conductive coatings which could be applied to PHGMs to combine the effects of porous and conductive additives [21,22]. Electroless deposition of SnO_x –Sb coatings for enhancing electrical conductivity has also been successfully implemented [23].

This paper presents the experimental results of using porous, hollow, glass microspheres (PHGMs), as paste additives to improve the porosity of the active material in positive electrodes. Models previously developed for lead acid batteries are used to estimate the performance of electrodes having these additives. The goal of using PHGMs, which are nonconductive additives, is to increase electrolyte storage and porosity in the electrodes to improve active material utilization at high rates. These PHGM additives are only expected to improve active material utilization at the higher rates and, in fact, would be expected to reduce utilization at low rates because of the reduction in active material conductivity and the associated decrease in the CVF.

2. Experimental

2.1. Paste mixing procedure

Barton-type lead oxide was used for the paste. The various types of additives were added to the dry mix. Several minutes of dry mixing was done before any acid was added. A ratio of 30 ml of 1.4 g cm^{-3} sulfuric acid to 1 lb (0.453 kg) of lead oxide was added at a rate of approximately 3 ml per min to keep the paste from getting too hot. The mixing was done in a KitchenAid mixer. A 50 ml

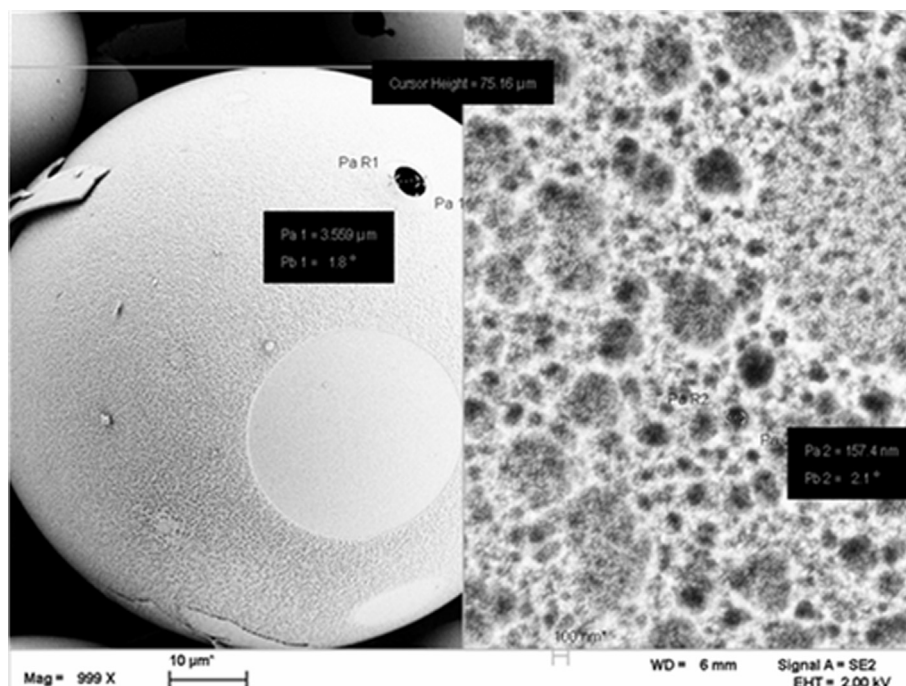


Fig. 1. PHGMs made from S38 HGMs after etching in 1% HF for 20 min. Close up of wall surface shows regular formation of submicron pores.

volume of deionized water was then added over approximately five minutes. Occasionally, the mixer would be stopped to scrape the sides of the bowl to ensure a homogeneous mixture. Small amounts of water (1–3 ml) were then added until the paste reached its maximum density before starting to decrease with additional water.

In formulating the paste, attempts were made to keep the active material porosity the same for all the plates and the technique we used to accomplish this goal was to stop adding water when the maximum density was reached. Paste without additives had a density of approximately 70 g in^{-3} (4.27 g cm^{-3}). Paste with additives, which are less dense than lead oxide, had a lower density. The density is measured by weighing the paste in a crucible that has a known volume. If additional water was needed for a better pasting texture, a minimal amount was used.

2.2. Cell fabrication

The grids and commercial production plates were purchased for these tests. The positive grids have the following specifications: 8.55 cm high, 9.27 cm wide, 0.114 cm thick, and having a weight of $21 \pm 0.5 \text{ g}$. The negative grids were thinner (0.092 cm) with a weight of $17 \pm 0.5 \text{ g}$ but the other dimensions were all the same. The composition of the grids is considered irrelevant for the scope of these experiments. All plates were hand pasted on both sides to match the production plate thickness (0.13 cm) as closely as possible. After pasting, the plates were put through a roller press and then placed into a pressure cooker for approximately 24 h for curing. After curing, the plates were put into an oven that is kept at 37.8°C (100°F) for another 24 h to dry before assembly into cells.

At least three cells were made and tested for every type of plate. For the positive test plates, each cell contained one positive plate containing the additive, and two production negatives so that the positive plate was the limiting electrode. The positive plate was wrapped in a layer of glass mat having 90% porosity. It was then wrapped with two layers of polyethylene separator. Each assembled cell contained excess electrolyte which was monitored closely.

2.3. Formation and cycling procedures

A two-shot formation cycle was performed on these plates. The cell was filled with 1.1 g cc^{-1} of H_2SO_4 . The amount of amp-hours used for charging and discharging the cells was determined by the amount of active material in the positive plate, referred to as the stoichiometric capacity (CS). The positive paste had 0.2241 Ah g^{-1} and the negative paste had 0.2587 Ah g^{-1} of active material. Each cell was initially formed at the CS/48 rate and then finished at the CS/24 rate. The voltage limit was set at 2.65 V. The charge cycles ran until 125% of the stoichiometric capacity was reached. After the formation cycle finished, 1.1 g cc^{-1} acid was replaced with 1.3 g cc^{-1} and was conditioned for 9 cycles at the three hours rate. All charge and discharge cycles were performed with Arbin battery cycling equipment, and all tests were done at a constant temperature of 100°F (37.8°C) to eliminate any temperature based performance variation. The cell voltage, current, charge and discharge amp-hours were recorded for each step for each cell.

2.4. PHGM description

Several types of porous hollow glass microspheres (PHGMs) were investigated. The PHGMs are identified as SRNL (Savannah River National Laboratory) PHGMs, skinned PHGMs, porous S38 (PS38), and SRNL 600 HT's. The SEM pictures in Figs. 1–5 show the differences in the pore types for the various PHGMs tested. Fig. 1 shows the porous S38 PHGMs fabricated from the 3 M hollow,

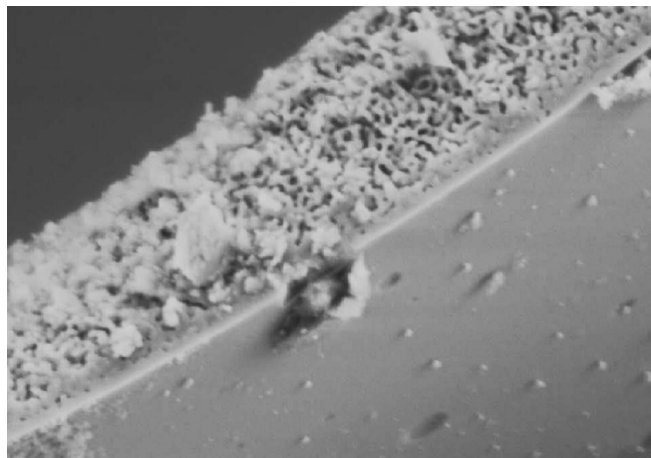


Fig. 2. Cross section of SRNL PHGMs.

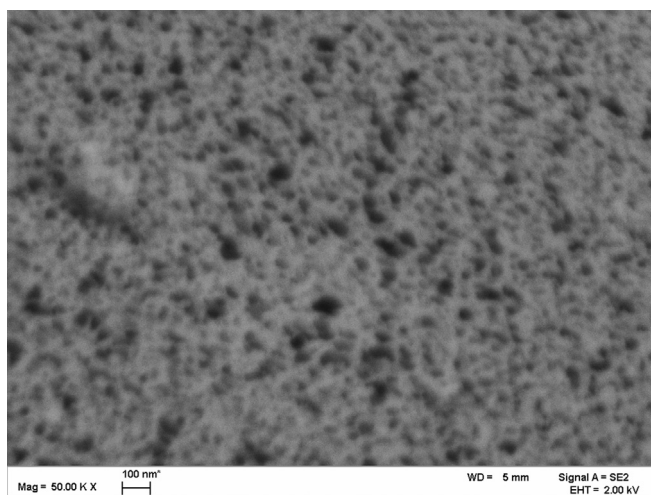


Fig. 3. Skinned PHGM surface (SRNL PHGM after being shaken for 15 min in 2% HF. The outer layer is no longer present.).

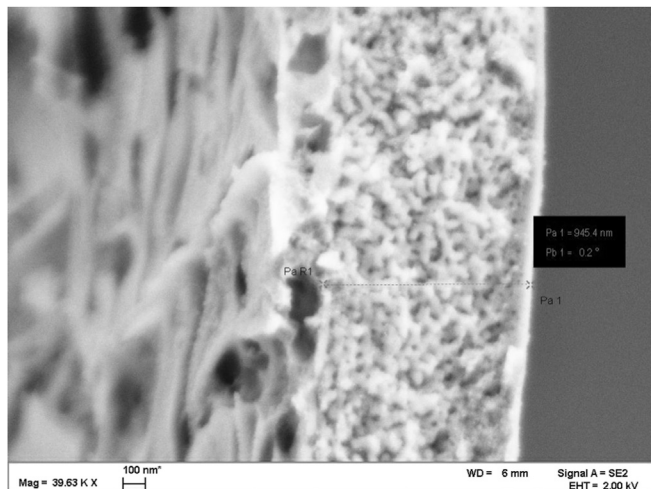


Fig. 4. SRNL 600 HT PHGM cross section.

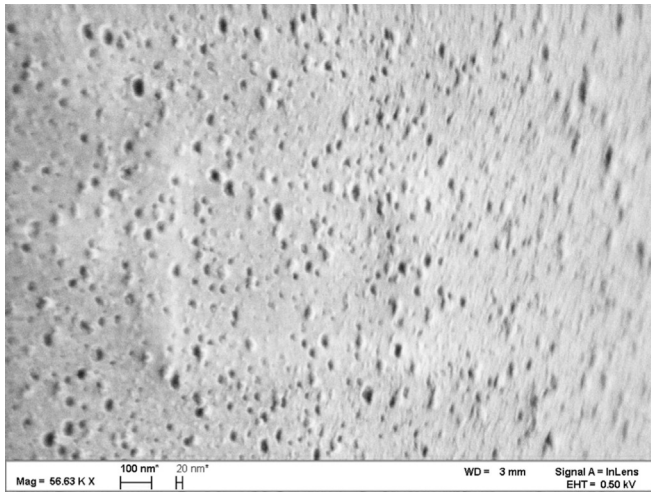


Fig. 5. SRNL 600 HT PHGM surface.

glass microspheres (HGMs) S38 product. The porous S38 PHGMs were created by soaking the S38 HGMs in a 1% hydrofluoric (HF) acid solution for 20 min and manually separating the sinkers, which fall to the bottom of the solution because they are porous, and floaters, which are removed because they are nonporous [13,14].

The surface of the porous S38, shown in Fig. 1, appears to have a very porous structure. The original SRNL PHGMs are shown in Fig. 2 and appeared to have an outside layer. In an attempt to skin or remove the outside layer on these PHGMs, they were shaken for 15 min in 2% HF. This process appeared to remove the outside layer on this PHGM type, see Fig. 3, but also caused additional breakage of the PHGM's. The third type of PHGM tested was processed by SRNL at a higher temperature to increase the pore size in the PHGM and are referred to as 600 HT. A cross section of the 600 HT PHGMs is shown in Fig. 4 and its surface is shown in Fig. 5. These 600 HT PHGM appeared to provide the best performance of all the PHGMs tested.

3. Results

3.1. PHGM plate models

Two types of models referred to as the conductivity model and the diffusion model are used interactively to predict the performance of plates having these additives. The conductivity model estimates the CVF of paste having additives like the HGMs, PHGMs, or conductive particles. The CVF estimated from the conductivity model is then used in the diffusion model to estimate the performance of cells at different rates of discharge. The CVF and the porosity are the two most important factors used in the diffusion model to establish plate performance. The diffusion model is a finite difference equation model that estimates the utilization of the battery under varying current loads. It can also be used to study the battery performance effects of porosity, CVF, diffusion rate, electrolyte concentration levels, plate thickness, separator thickness, and other battery parameters. A more detailed explanation of both the conductivity model and the diffusion model used in this paper is provided below.

A two-dimensional (2D) conductivity model was developed to calculate the critical volume fraction of electrodes having various conductive or non-conductive additives [24]. The model compares favorably with results published using percolation theory [5,6]. A three dimensional (3D) model was subsequently developed and

evaluated [25]. Although this model expanded the model from 2D to 3D, the 3D model did not account for porosity. A 3D model based on the simple cubic centered (SCC) lattice that included porosity was created [26] to overcome this problem. This model was later extended to include different lattice structures [27]. Although the 3D model with porosity is much more complex than the 2D model, the final 3D model [27] for physically realizable lattice structures and a porosity of 50% return CVF results very similar to the 2D model [24]. Because of the similarity of these results, the simple 2D model is used to estimate the CVF for the PHGM plates.

The CVF for the PHGM plates is used in the diffusion model to estimate the performance of these plates. We use a one-dimensional, finite difference diffusion model [28–30] to evaluate the performance of the standard and additive plates at different discharge rates. The initial diffusion models [28,29] were later improved with the use of a numerical fast splitting method [30] for efficiently generating discharge profiles. The equations solved by the model include Fick's Law, the Nernst equation, and the Butler–Volmer equation. The diffusion model is used later in this paper to estimate and analyze the discharge performance of the PHGM plates.

The 2D conductivity model consists of an array of nodes arranged in a structure as shown in Fig. 6. The model uses a Monte Carlo method to randomly evaluate the nodes of the electrode. Each node in the model is connected to eight other nodes and therefore has a coordination number of eight. The model randomly selects a test node and then searches for a conductive pathway to the edge of the node matrix which represents the grid. If the model finds a conductive pathway, the test node is considered “discharged”, is marked as such, and can no longer be used in a pathway. If the model cannot find a conductive pathway then the test node is marked as “isolated.” In this fashion, every node will either be discharged or isolated at the end of discharge.

Once all the nodes have been marked as either discharged or isolated, the model reports the utilization: the number of nodes discharged divided by the total number of nodes. Additives are modeled as nodes that are permanently either non-conductive or conductive depending on the additive type, cannot be discharged, and are not included in the CVF calculation. For our simulation, the PHGMs are made of glass and are considered non-conductive additives.

Fig. 7 shows the utilization predicted by the model when either conductive or non-conductive additives are included in the electrode [24]. Conductive pathways in the active material are vital to allow electrons to move to the reaction site in a plate. As expected, the model shows that including conductive additives in the

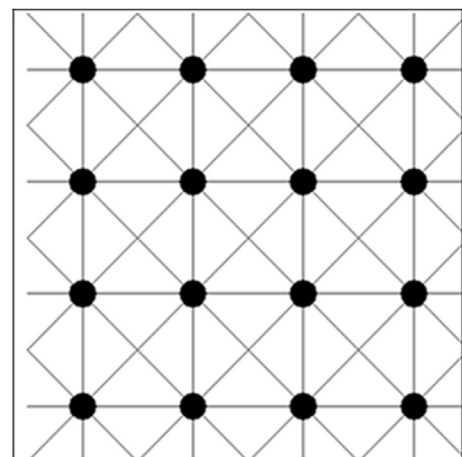


Fig. 6. Graphical depiction of the node structure used in the model.

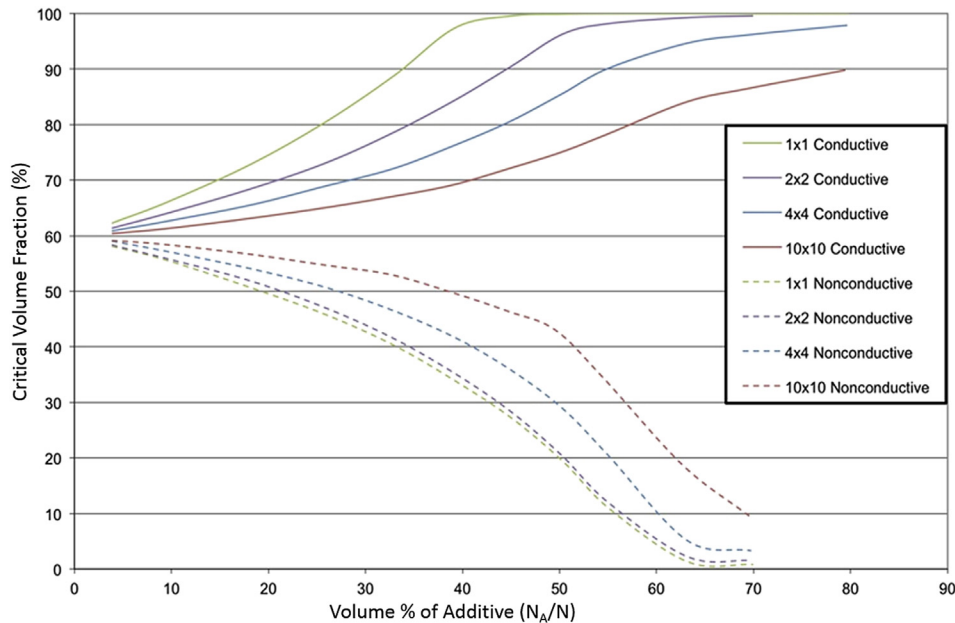


Fig. 7. Critical volume fraction predictions for spherical shaped conductive and non-conductive additives of varying sizes vs. the node volume% additive, N_A/N .

electrode improves the CVF while, conversely, non-conductive additives worsen the CVF. However, the size of the particle also has an effect; large particles have less effect on the CVF than do small particles. The simulation results shown in Fig. 7 indicates that the greatest improvement comes from using small conductive additives, while the least detriment comes from using large non-conductive additives.

The results of this model shows that both negative and positive plates having no additives can achieve a 60% critical volume fraction. In reality, the critical volume fractions of the negative and positive hand pasted plates are 58% and 48%, respectively. Bode estimates the experimental average for negative plates to be approximately 60% and positive plates 55% [1]. Using the node volume percent of additive N_A/N , and the average particle size (1×1 , 4×4 , 10×10 etc.), a predicted critical volume fraction can be read from the chart in Fig. 7.

By analyzing several three dimensional lattice structures in previous work [26,27], the node size was estimated to be between 1 and 10 μm . In our present work, the model used a node size of approximately 5 μm . The glass spheres have an approximate average diameter of 20 μm and are therefore modeled as a 4×4 square of non-conductive nodes. Note that the larger additive not only replaces nodes but also displaces some of the porosity surrounding the nodes, as shown in Fig. 8.

Due to the nature of the model, the critical volume fraction, as shown in Fig. 7, is referenced to a *node volume percent*, N_A/N . The *node volume percent* must take into account any displaced porosity by the additive. The following empirical equation, Eq. (1), was adopted to help estimate the percentage of nodes shown in Fig. 7 that would be replaced by the additives.

$$\frac{N_A}{N} = \frac{1}{n} f_S + \frac{n-1}{n} f_T \quad (1)$$

In Eq. (1), N_A is the number of nodes displaced by additives, N is the total number of nodes in the plate model, n is the ratio of the average additive diameter to the active material node diameter, and f_S and f_T are the fractions defined in Eqs. (2) and (3).

Because the displaced porosity depends on additive size, the node volume percent equation requires the use of two volume

fractions, f_S and f_T . The *additive solid volume fraction*, f_S , is the amount of additives in the mix compared only to the volume of the solids and is given by the following equation:

$$f_S \equiv \frac{V_{AD}}{V_{AD} + V_{AM}} \quad (2)$$

where V_{AD} is the true volume of the additives, and V_{AM} is the true volume of the active material. Because these volumes can be determined by dividing the mass of the additives or active material by their true density, f_S is known at the time of mixing. For this reason, the *additive solid volume percent* (i.e. $f_S \times 100\%$) is used to identify different batches of battery paste. We often refer to this volume percentage as the additive loading.

The second volume fraction is the *additive total volume fraction*, f_T . This fraction relates the volume of the additives to the total volume of the electrode, V_T , including the porosity and is found with the following equation:

$$f_T \equiv \frac{V_{AD}}{V_T} \quad (3)$$

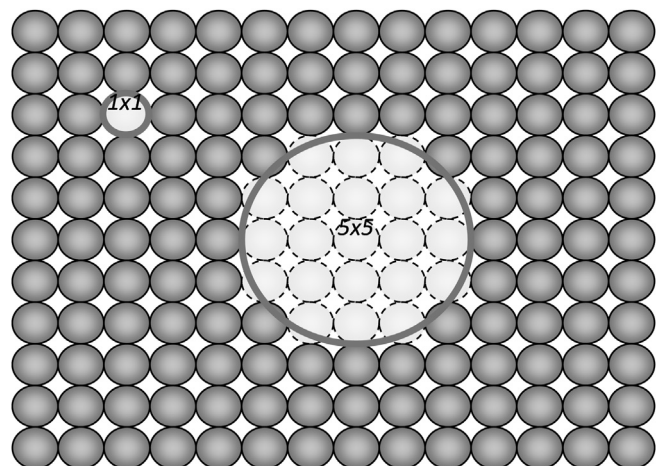


Fig. 8. Example of connected node network with small and large additives.

The fraction f_T is undetermined during pasting because the porosity is unknown. The value of V_T must be estimated from the masses of the constituent parts and the plate's porosity once the plate has been cured.

Once these volume fractions are defined, the rationalization for Eq. (1) can be explained. Eq. (1) was developed so that when $n = 1$ and the additive size and node size are identical; the number of nodes replaced by the additives is the same as the volume of additives. Therefore, when $n = 1$, the number of additive nodes are equal to the number of active material nodes replaced and the node fraction is equal to f_S . When n is large (i.e. $n \geq 10$), the additives are much larger than the active material nodes and they therefore displace porosity as well as active material nodes as shown in Fig. 8.

For large additives, the ratio of active material nodes replaced by additive nodes will approach f_T (i.e. if $n \geq 10$ then, $N_A/N \approx V_{AD}/V_T$). Assuming 50% porosity, large additives only displace about half as many active material nodes as small additives when $n = 1$. Eq. (1) therefore reduces to the appropriate ratios expected for small additives ($n = 1$) and for large additives ($n \geq 10$). Typically n is between 1 and 5 for the additives discussed in this report. Although the empirical mathematical relationship provided by Eq. (1) is only approximate, the equation does provide a simple and a relatively accurate estimate for the node volume percent used in the conductive model for all additive sizes. When f_S , f_T , and n are known, then N_A/N can be calculated from Eq. (1) and the CVF for the plate with additives determined from Fig. 7.

Using the relationship for the number of nodes displaced by additives in our conductivity model, Eq. (1), the porosity of the plates having either HGMs or PHGMs can be estimated. In order to estimate the total porosity, P , of PHGM additive plates, we first derive the porosity of the plate, P_A , where the internal volume of the PHGMs is not included. This porosity would be the same as if the PHGMs were non-porous or HGMs.

For this derivation, we assumed that the porosity of the active material that surrounds the additives is equivalent to the standard porosity, P_S , or the porosity of a plate without additives:

$$P_S = \frac{V_{P_{Std}}}{V_T} \quad (4)$$

where $V_{P_{Std}}$ is the volume of the porosity inside of a standard plate. The porosity of a plate with additives, P_A , is related to the porosity of the standard plate by finding the change in porous volume related to the additives, ΔV_P

$$P_A = \frac{V_P}{V_T} = \frac{V_{P_{Std}} - \Delta V_P}{V_T} = P_S - \frac{\Delta V_P}{V_T} \quad (5)$$

The reduction in porous volume associated with the additives is related to the difference between the volume of the additives and the volume of the nodes the additives replace. This is a key relationship for estimating the porosity and is shown in Eq. (6).

$$\frac{\Delta V_P}{V_T} = f_S - \frac{N_A}{N} \quad (6)$$

In Eq. (6), the additive solid volume fraction, f_S , represents the fraction of the solid volume that is occupied with additives and is determined experimentally. The fraction of nodes associated with additives in the model is given by N_A/N as found using the ad-hoc Eq. (1). When the nodes are small, the reduction in porosity will also be small since additives are similar in size to the nodes. When $n = 1$, Eq. (1) says that the nodes are the same size as the additives and N_A/N equals f_S so there is no reduction in porosity. Therefore, Eq. (6) is a fusion of the experimentally measured and the empirically estimated numbers associated with the conductivity model.

In order to simplify the derivation of ΔV_P a relationship between f_S , f_T , and P_A can be established. The electrode has three constituents: the additives, the active material, and the porosity of the active material. This gives an expression for the total volume V_T .

$$V_T = V_{AD} + V_{AM} + V_P \quad (7)$$

In the above equation V_P is the volume of the porosity of the electrode that is not associated with the internal volume of the additive, and is independent of the porosity of the additive. Using the definitions for f_T , f_S and Eq. (4) to solve for the solid volumes, $V_{AD} + V_{AM}$, an expression can be derived that relates all these quantities.

$$f_T = \frac{V_{AD}}{V_T} = \left(\frac{V_{AD}}{V_{AD} + V_{AM}} \right) \left(\frac{V_T - V_P}{V_T} \right) \quad (8)$$

$$f_T = f_S(1 - P_A)$$

By substituting the value for N_A/N from Eq. (1) and f_T from Eq. (8) into Eq. (6) and simplifying, we get the expression:

$$\frac{\Delta V_P}{V_T} = f_S - \left(\frac{1}{n} f_S + \frac{n-1}{n} f_S(1 - P_A) \right) = \frac{n-1}{n} f_S P_A \quad (9)$$

Substituting the value of $\Delta V_P/V_T$ from Eq. (9) into Eq. (5) and solving for P_A yields the following expression:

$$P_A = P_S - \frac{n-1}{n} f_S P_A \quad (10)$$

$$P_A = \frac{P_S}{1 + \frac{n-1}{n} f_S}$$

The above expression, Eq. (10), represents the porosity of the plate with additives not including the internal volume of the PHGM additives. We see when $n = 1$, that the porosity of the additive plate is equal to the porosity of a standard plate or $P_A = P_S$. When n is large, the porosity is reduced because the additives also displace porosity and not just the active material.

It should be noted that an implicit assumption in our model is that the small, active material nodes define the electrode's structure so that f_S is restricted to having values less than one-half. For additive volumes greater than 50%, the additives contact other additives so that they dominate the electrode structure and not the active material. For a more general discussion on binary sphere mixtures, see Ref. [31].

To find the total porosity, P , we only need to add the internal volume of the PHGM additives to the value P_A derived in Eq. (10). The following equation, Eq. (11), provides the total porosity of the plate with additives including porosity inside of the additives.

$$P = P_A + Z f_T \text{ or } P = P_A + Z f_S(1 - P_A) \quad (11)$$

In Eq. (11), Z is the porous fraction of the PHGM additive available for electrolyte storage. The value of Z for the PHGM additive used in this paper was 0.85 (i.e. determined from true density of microsphere to density of glass) while the value of Z for the non-porous HGMs would of course be zero.

In Fig. 9, the curves for P_A , Eq. (10), and P , Eq. (11), are plotted for various values of n and with $Z = 0.85$. The porosity of the standard plate, P_S , was chosen to be 0.5 and can be inferred from the figure as the y-intercept for all the plates when the additive loadings are zero. This value for P_S is an approximate value for the porosity of formed plates. Fig. 9 shows that for small additives, the decrease in porosity is low. In fact, plates having additives with $n = 1$, have no loss in porosity. However, the small additives have the biggest effect on the conductivity and CVF as shown in Fig. 7. Alternatively, the

larger size additives have a larger effect on porosity, Fig. 9, but a much lower effect on conductivity and the CVF, Fig. 7. Previously, researchers used the porosity for plates having HGMs to be approximately 50%. Although this assumption seemed reasonable at the time for small loadings of additives, the present analysis along with experimental data suggests that the larger HGM and PHGM additives do decrease porosity. This effect should be included when evaluating high rate performance of plates having these additives.

At low rates where diffusion and porosity is not very important, the 50% porosity assumption would not be expected to change the results. However, at high rates both the porosity and CVF of the plates should be calculated and modeled. Knowing the approximate size of the additive being evaluated (i.e. $n = 4$ for the PHGMs used in this paper), the additive solid volume fraction, f_s , determined experimentally, and the porosity of the standard plate (i.e. $P_s = 0.5$), then P_a can be calculated with Eq. (10). The CVF and the porosity, P , of the plate can then be determined from N_a/N using Eq. (11) and $Z = 0.85$. These values are used to model the performance of the plates having PHGM additives, see Fig. 9.

In the following sections, we will either measure or estimate all the above parameters for plates having PHGM additives. Because the primary reason for using PHGMs in plates is to increase porosity, an attempt was made to either measure or estimate the porosity of the plates at every step of the fabrication and forming process. Due to inexperience, researchers did have difficulty in pasting and fabricating plates having PHGMs. These difficulties included the ability to mix the PHGMs into the paste, fill the PHGMs with electrolyte, and form the plates with the non-conductive PHGM additives. In addition, we also had concerns about the ionic transport through the walls of the PHGMs once they were filled. The results will be discussed while addressing these possible problems.

3.2. PHGM porosity test results

The plates tested in this project were loaded with varying amounts of PHGMs. The loadings were all based on the additive solid volume fraction, f_s , as provided by Eq. (2). This volume ratio provides a measurement of the amount of additives being used while the paste is being prepared. The additive total volume fraction, f_t , as described in Eq. (3), cannot be established until after the

plate is fabricated and varies according to the amount of water added to the mix during fabrication and the final porosity of the plate. Both additive fractions, f_s and f_t , are needed to correlate the experimental data to the models previously discussed in the “PHGM plate model” section.

All the PHGM spheres had a density of 0.296 g cc^{-1} , which was assumed for all of the additives except the skinned PHGMs. The density for the skinned PHGMs was assumed to be approximately two thirds the densities of the original PHGMs or about $(0.200 \text{ g cc}^{-1})$. The density of the K25 HGM used in these calculations was 0.25 g cc^{-1} . A range of approximately 11%–43% of additive volume to solid material volume was tested and compared to standard hand pasted plates. PHGM additives were only added to positive plates.

The primary purpose for including PHGMs in the active material of lead acid batteries is to increase the porosity of plates and hence their high rate performance. Tables 1 and 2 provide the plate parameters for both the cured and formed plates, respectively. The type of paste is provided in the first column and the amount of additive loading in the paste is indicated in the second column of both tables. The additive loading is the amount of additive volume to the total volume of solids (i.e. f_s in Eq. (2)). This ratio is used to formulate the paste and can be calculated at the beginning of the process. In addition, the mass of all the other paste constituents is also recorded including the final paste density. The weight of each hand pasted plate is recorded so that the mass and number of moles of the lead oxide, free lead, sulfuric acid, and water is known for each plate. A free lead content of 11% for the Barton type lead oxide was chosen from experimental analysis and because this amount matches the experimental data on the cured standard plate weights. This information was used to estimate the lead sulfate and lead oxide hydrate of the cured plate as discussed below.

Weight measurements were the basis for all the calculated parameters shown in Table 1. These measurements included the weight of each pasted plate, cured plate, and soaked cured plate as well as the weight of all the constituent components of the wet paste. The cured paste was modeled as a combination of two lead oxide hydrate ($2 \cdot (\text{PbO}) \cdot \text{H}_2\text{O}$) and lead sulfate (PbSO_4). We assumed that all the sulfuric acid in the wet paste of a plate would react with the lead oxide to form lead sulfate and that the remainder of the lead oxide would form hydrate. This analysis method provided a very good estimate for the weight of the cured plates (i.e. Column 4, Table 1) to the measured cured plate weights for both the standard plates (i.e. measured 32.91 g vs. estimated 33.03 g) and HGM plates (i.e. measured 31.58 g vs. estimated 31.64 g). These numbers are extremely close and represent an average difference of only 0.12 g for nine standard plates with a standard deviation of $\pm 0.39 \text{ g}$ and 0.07 g for five HGM plates with a standard deviation of $\pm 0.26 \text{ g}$. The model's estimates for both types of cured plate weights are less than 0.5% of the measured values. As previously noted a free lead content of 11% for the Barton type Lead oxide was used to help match the experimental data with the cured standard plate weights. However, all the assumptions used with the standard plates also worked very well with the HGM plates and helps validate both the assumptions and method employed in this analysis.

The method employed for estimating the porosity of the cured plates was to measure the mass of the cured plate after drying, and then to measure the mass of the plate after it was soaked in de-ionized water to fill all the pores. For the standard and HGM plates, the difference between these two masses is the total water absorbed in the plate (i.e. Column 8, Table 1) and represents the active material porosity volume for these plates. However, the total volume of the plate, V_t , must also be estimated before the plate porosity (i.e. porosity volume/plate volume) can be determined. The volume of all the constituents in the plate can be used to

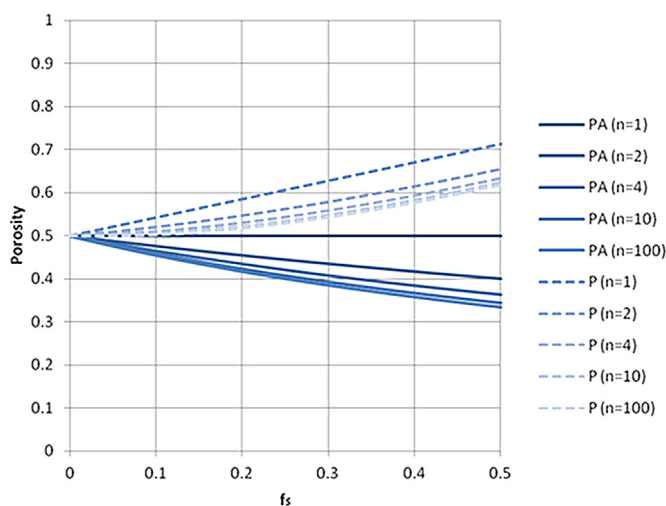


Fig. 9. Theoretical porosities for paste including additives. P_a is the porosity not including additive porosity. P is the total porosity including the internal additive volume.

Table 1

Model parameters for each plate type after curing process.

Cured paste	Additive solid volume fraction (f_s)	Additive total volume fraction (f_r)	Plate thickness (in)	Estimated active material mass (g)	H ₂ O PHGM volume (cc)	Additive water fill ratio	H ₂ O active material (cc)	H ₂ O total (cc)	Active material porosity	Total porosity	Figure of merit (cc g ⁻¹)	Figure of merit ratio
Standard paste	0.0%	0.0%	0.0444	33.03	0.00	0.00	2.50	2.50	35.3%	35.3%	0.076	1.000
HGMs	13.2%	6.1%	0.0458	31.64	0.00	0.00	2.54	2.54	34.7%	34.7%	0.081	1.069
SRNL PHGMs (processed) ^a	35.4%	17.8%	0.0417	23.11	1.06	0.78	2.31	3.38	42.2%	50.7%	0.146	1.934
SRNL high temp PHGMs	11.6%	5.3%	0.0467	32.61	0.34	0.63	2.67	3.01	37.1%	39.6%	0.092	1.218
SRNL high temp PHGMs	36.9%	19.3%	0.0484	28.10	1.29	0.81	2.55	3.85	39.9%	48.6%	0.137	1.811
SRNL high temp PHGMs	43.9%	26.2%	0.0423	24.32	1.49	0.60	1.63	3.12	33.1%	46.7%	0.128	1.698
Porous S38	15.2%	7.2%	0.0443	30.23	0.43	0.35	2.43	2.86	36.7%	40.1%	0.094	1.247

^a Note: This has been modeled with smaller PHGM density, $D = 0.2$, and more internal PHGM volume, $Z = 90\%$.

estimate the total volume of the plate. Unfortunately, the exact constituents for the cured plate including the amount of tribasic and tetrabasic lead sulfate were not known. A simple assumption for the standard and HGM plates was therefore made that the total volume of the plate, V_T , includes the volumes of the two lead oxide hydrate ($2 \cdot (\text{PbO}) \cdot \text{H}_2\text{O}$), the lead sulfate, and the volume of the water used to estimate the porosity volume. For the HGM plates, the volume of the HGM additives must also be included. The total volume of the PHGM plates is similarly estimated by subtracting the additional weight of the water inside the PHGMs from the soaked plate weight before making the same volume calculation as with the standard and HGM plates. The thickness of the plate (i.e. Column 3, Table 1) and the additive total volume fraction, f_r , (i.e. Column 2, Table 1) can be calculated from this estimate for V_T .

Knowing V_T also allows the porosity of both the hand pasted standard and the HGM plates to be estimated (i.e. total H₂O volume/ V_T). Again, modeling the cured paste as a combination of lead oxide hydrate, lead sulfate, and HGM additives allows the cured plate porosities to be estimated and compared with experimental data. The estimated value for the porosities of the cured plates (i.e. Columns 9 and 10, Table 1) is very close to the measured cured plate porosities for both the standard plates (i.e. measured 0.356 vs. estimated 0.353) and the HGM plates (i.e. measured 0.342 vs. estimated 0.347). Again, these are extremely close and are a result of the good agreement between the measured and estimated dry, cured plate weights.

Unfortunately, the method for measuring the water volume in the cured plates did not work for plates with the PHGMs. The problem with these additives is that they are hard to dry. We initially were not able to make any sense from the measured

weights of the cured PHGM plates until we finally realized that not all the internal volume of the PHGMs were dry. However, as previously mentioned, the weights of the saturated PHGM plates were accurate and so we used these numbers to calculate the total volume, V_T , and porosities for all the PHGM plates. Again, the cured PHGM plate was assumed to consist of lead oxide hydrate and lead sulfate which allowed us to estimate the weight and volume of the active material mass (i.e. Column 4, Table 1). By subtracting off this same weight (i.e. the lead oxide hydrate and sulfate) along with the weight of the PHGMs, we were able to estimate the total amount of water stored in the cured, soaked plate (i.e. Column 8, Table 1). Subtracting off the water stored in the plate's PHGMs (i.e. Column 5, Table 1) from the total amount of water in the plate provided an estimate for the amount of water stored in the active material (i.e. Column 7, Table 1). The active material porosity (i.e. Column 9, Table 1) can be calculated by dividing the amount of water stored in the active material by the volume of the sum of this water and the active material volume. The total porosity of the plate (i.e. Column 10, Table 1) includes both the porosity of the active material as well as the internal volume of the PHGM.

As a check on these calculations, we estimated how much water remained in the PHGMs after “drying” and compared it to the total amount possible (i.e. Column 7, Table 1). Our calculations on the PHGM plates only made sense when we included water in the PHGMs to account for the added weight in the “dry” cured plates. We found that this ratio was between 0.35 and 0.81 which was reasonable as all the PHGMs appeared to be partially filled. The total porosity (i.e. Column 10, Table 1) includes both the porosity in the active material, denoted as active material porosity, and the porosity in the PHGMs, which is assumed to include the entire

Table 2

Average estimates for each of the various plate types after formation cycles.

Formed paste (Estimate)	Additive active material f_s	Additive total volume f_r	Plate thickness (in)	Active material mass (g)	H ₂ O PHGM volume (cc)	Additive water fill ratio	H ₂ O active material (cc)	H ₂ O total (cc)	Active material porosity	Total porosity	Figure of merit (cc g ⁻¹)	Figure of merit ratio
Standard paste	0.0%	0.0%	0.0444	32.81	0.00	0.00	3.43	3.43	48.5%	48.5%	0.105	1.000
HGMs	13.2%	6.1%	0.0458	31.43	0.00	0.00	3.43	3.43	49.8%	46.8%	0.109	1.043
SRNL PHGMs (processed) ^a	35.4%	17.8%	0.0417	22.95	1.06	1.00	2.96	4.02	54.0%	60.4%	0.175	1.675
SRNL high temp PHGMs	11.6%	5.3%	0.0467	32.39	0.34	1.00	3.59	3.93	49.9%	51.8%	0.121	1.159
SRNL high temp PHGMs	36.9%	19.3%	0.0484	27.91	1.29	1.00	3.33	4.63	52.2%	58.5%	0.166	1.585
SRNL high temp PHGMs	43.9%	26.2%	0.0423	24.16	1.49	1.00	2.30	3.79	46.8%	56.8%	0.157	1.499
Porous S38	15.2%	7.2%	0.0443	30.03	0.43	1.00	3.28	3.71	49.6%	52.1%	0.123	1.180

^a Note: This has been modeled with smaller PHGM density, $D = 0.2$, and more internal PHGM volume, $Z = 90\%$.

internal volume of the PHGMs in a plate. The active material and internal PHGM volumes are then summed to determine the total porosity for the cured plate which is used to calculate a figure of merit for the plate. The last two columns in Table 1 provide a figure of merit for all these different porosity additives.

The figure of merit used for these porous additive plates is the volume of electrolyte that can be stored in these plates (i.e. the total porosity of the plates) divided by the amount of active material in the plate (i.e. Column 11, Table 1). The figure of merit can be improved significantly with the PHGM additives. For example, the skinned PHGM plates had a figure of merit almost twice that of the standard plates (i.e. 0.140 cc g^{-1} to 0.076 cc g^{-1}). When PHGMs are added to the paste, they both increase the porosity and reduce the active material, so both these will increase the figure of merit. For comparison purposes, the figure of merit can be standardized with the figure of merit for the standard plate resulting in a figure of merit ratio that is shown in the last column of Table 1 (i.e. Column 12).

During formation we assume that the lead oxide hydrate and lead sulfate is converted to lead dioxide (PbO_2). The weight and volume of each of these components will decrease when converted to lead dioxide. However, the plate volume is assumed to remain the same so that a reduction in the active material volume will result in an identical increase in the porosity volume. As shown in Table 2, the weight reduction is reflected in an insignificant lower active material weight (i.e. Column 4, Table 2) from the cured weight but a significant increase in the porosity volume of the active material (i.e. Column 7, Table 2).

When the cured plate is formed, the active material porosity increases (i.e. Column 9, Table 2) as does the total porosity volume of the plate (i.e. Column 8, Table 2) and the plate's total porosity (i.e. Column 10, Table 2). These changes are reflected in higher figure of merits (i.e. Column 11, Table 2) for all the formed plates including the standard plate. The figure of merit ratios (i.e. Column 12, Table 2) is also modified from those for the cured plates, Table 1. Because the standard plate's porosity improved more than the other plates having additives after formation, the figure of merit ratios for the formed plates, Table 2, were lower than for the cured plates, Table 1.

The figure of merit ratios is summarized in Table 3 for both the cured and formed plates. The standard plates have a figure of merit ratio of 1.00 and the other plates with additives have higher ratios, with the highest ratio for the formed plates being 1.675. The additives increase the amount of porosity and hence the volume of electrolyte stored in the plates. More electrolyte stored in the active material and better diffusion in the plates will help improve the high rate performance of these plates. Plates having a high figure of merit should provide superior performance at high rates. However, at lower rates the performance may be reduced due to a decrease in the CVF of the plate that occurs when you add non-conductive additives. The increase in porosity as well as the decrease in the

CVF is included in the models used later in this section to predict the performance for all the plates.

In Table 4, a comparison is provided between the modeled porosity equations, Eq. (10) for P_A and Eq. (11) for P , and the porosity estimated from the experimental data for each of the plates described in Table 2. Although Eq. (1) and the equations derived from it, Eqs. (10) and (11), are all based on simple idealizations of the active material, the experimental data has good agreement with these equations. The experimental porosity for the standard plates (i.e. $P_S = 48.5\%$) is used in both equations so that they are forced to fit the experimental data at that point. A comparison between the equations modeling the porosity and the measured porosity of the cured plates of Table 4 is plotted in Fig. 10. The lower blue (in the web version) line in the figure is the active material porosity of the plate, P_A , which does not include the internal porosity of the PHGMs. The total plate porosity, P , which includes the added internal porosity of the PHGMs is shown as the green (in the web version) line that lies across the top of the plot.

The experimental porosity data is also plotted in Fig. 10 in order to provide a visual comparison between the equations and experimental porosity measurements. The circular data point is the average porosity of the standard positive plates. The X data point represents the average porosity of the HGM positive plates. The square data points are the average measured total porosities, P , of the PHGM plates. The triangular data points represent the active material porosity, P_A , of the plates. The active material porosity is also the same as the total porosity for the Standard and HGM plates. For the PHGM plates, the active material porosity is the same as the total porosity minus the internal volume of the PHGMs. The model for our PHGMs uses the size parameters of $n = 4$, and $z = 0.85$. The exception to this rule is for the skinned PHGM plates (at 35.4% on the x axis) which use $z = 0.9$, as well as the HGM plates (at 13.2% on the x axis) which, of course, has no internal volume and therefore uses $z = 0$. The error bars that represent the standard deviation for the different plates are small and are also shown with the data along with the average value. We note from Fig. 10 that the model estimates the porosities for all the plates surprisingly well and provides a general trend line relating plate porosity with the amount of porosity additives.

3.3. Discharge test results for PHGM plates

In this section, the experimental results of a number of PHGM plates discharged at different rates will be reported along with results from the model used in the previous section. At least three plates of each loading were tested at various discharge rates. Excess electrolyte and negative material were used so that the positive plate with the additives would be the limiting electrode. To provide a control group for the experiment, production plates and hand pasted standard plates were cycled to provide a comparison with the performance of the plates with additives.

Table 3
Average figure of merit for different plate types.

		Standard	HGM (13.2%)	600 HT (11.6%)	600 HT (36.9%)	600 HT (43.9%)	Skinned PHGMs (35.4%)	Porous S38's (15.2%)
Cured plate	Water volume to active material mass (cc g^{-1})	0.076	0.081	0.092	0.137	0.128	0.146	0.094
	Additive ratio	1.000	1.069	1.218	1.811	1.698	1.933	1.247
	Standard ratio							
Formed plate	Water volume to active material mass (cc g^{-1})	0.105	0.109	0.121	0.166	0.157	0.175	0.123
	Additive ratio	1.000	1.043	1.159	1.585	1.499	1.675	1.180
	Standard ratio							

Table 4

Tested PHGM positive plates with modeled and measured porosities.

Plate type	Additive% of solids volume	Additive size ratio n	Plate porosity in active material (P_A)		Total plate porosity (P)	
			Model	Measured	Model	Measured
Standard positive plate	0.0%	N/A	48.5%	48.5%	48.5%	48.5%
Porous S38 (Pos)	15.2%	4	43.5%	46.0%	50.8%	52.1%
600 HT (Pos)	11.6%	4	44.6%	47.3%	50.1%	51.8%
600 HT (Pos)	36.9%	4	38.0%	42.1%	57.4%	58.5%
600 HT (Pos)	43.9%	4	36.5%	34.5%	60.2%	56.8%
Skinned SRNL (Pos)	35.4%	4	38.3%	44.4%	56.9%	60.4%
K25 HGMs (Pos)	13.2%	4	44.1%	46.8%	44.1%	46.8%

Before a plate's discharge performance can be modeled, the critical volume fractions, CVF, must be determined and combined with the plate porosities shown in Table 4. In Table 5, the parameters needed in Eq. (1) to calculate the *node volume percent*, N_A/N , are provided. These parameters include the two volume fractions, f_s and f_t , and n , the ratio of the average additive diameter to the active material node diameter. Once the *node volume percent* is known, the critical volume fraction for each plate can be determined from Fig. 7. This value is the non-scaled critical volume fraction which predicts that plates without additives will have a 60% CVF. The predicted critical volume fraction (CVF) is found by scaling down from 60% to 48%, the observed CVF for positive plates.

A simple method is used to scale the model's predictions for the positive plates, see Ref. [7]. The CVF value from Fig. 7, $CVF(X\%)_{Table}$, is multiplied by the ratio of CVF (0%) to 60% where CVF (0%) is 48% for positive plates as shown in Eq. (12).

$$CVF(X\%) = CVF(X\%)_{Table} \frac{CVF(0\%)}{60\%} \quad (12)$$

The scaled critical volume fraction is given for a number of plates in the last column of Table 5. These CVF values will be used to

model the discharge performance of the plates where the active material node size is estimated to be approximately $5 \mu\text{m}$ [26,27]. All the additives are approximately four times the node diameter for the active material (i.e. $n = 4$). In Fig. 11, both the original and scaled estimates are provided for the critical volume fraction (CVF) for all the plates tested.

The utilization predicted by the model for a number of additive plates at different discharge rates is shown in Fig. 12. Although all the data shown in the figure was generated from the model, experimental tests were also performed on these PHGM plates and are shown in Fig. 13. The discharge rates corresponding to the experimental ones shown in Fig. 13 are marked in Fig. 12 as "Approximate Discharge Range for Tests" and correspond to discharge rates of approximately 1C (1 h), 2C (1/2 h), 4C (1/4 h), and 10 A rates.

As observed in Fig. 12, the best performing plates were those with the highest figure of merit, Table 3. The model estimated the effect that both the higher porosity and the reduction in CVF had on utilization performance. The HGM plates had the lowest figure of merit and performed almost identical to the standard paste mix except at very high rates. Any improvement in utilization associated with the ratio of electrolyte to active material in the HGM plates appear to have been eliminated as a consequence of the lower CVF of the plates due to the non-conductivity of the additives. At the higher discharge rates, the model predicts that all of the additive mixes would outperform the standard paste. At the other extreme, the very low discharge rates, the model predicts that the PHGM cells would have lower critical volume fractions and utilizations than the standard cells. We see that the utilization is reduced at the low rates as more additives are incorporated into those plates.

The plates were discharged at four rates approximating the 1C, 2C, 4C, and 10 A rates. The 10 A rate was the maximum current for our single cell cycling equipment and was a higher rate than the 4C rate. The specific current used for each of the discharge rates was derived from the theoretical stoichiometric capacity of the positive plates using the following equation:

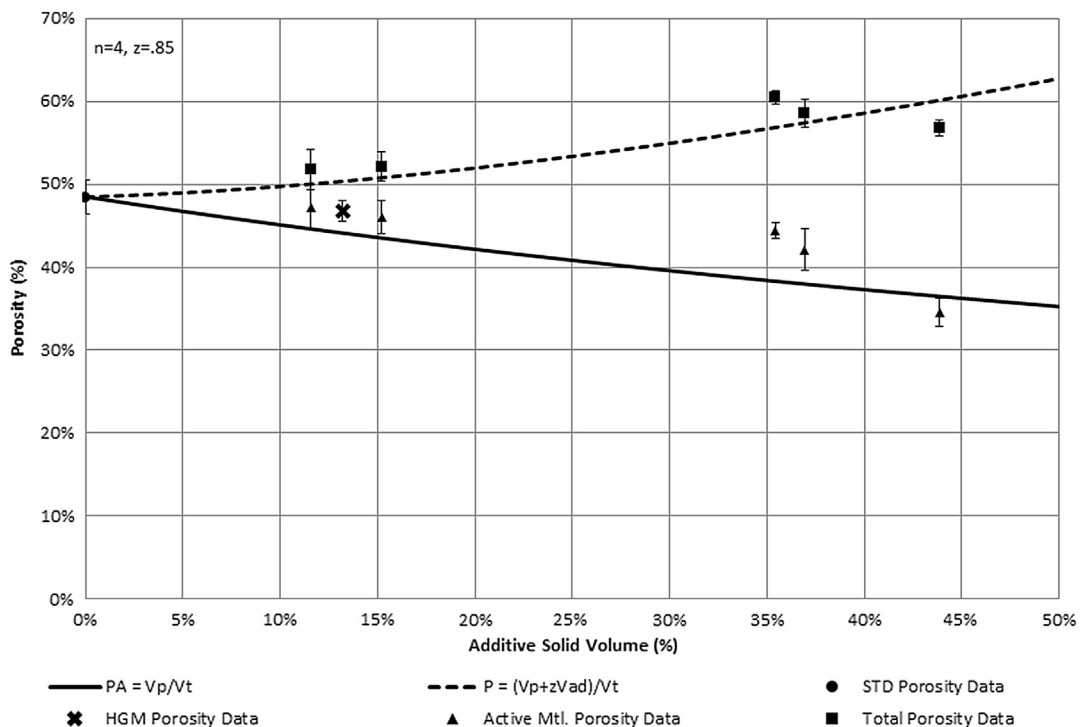


Fig. 10. Comparison of porosity model (solid lines) to the porosity data (data points) estimated from measured mass data.

Table 5
Scaled critical volume fraction predictions.

Plate type	Additive% of solids volume (f_s)	Additive% of total volume (f_r)	Additive size ratio (n)	Node volume% (N_A/N)	Non-scaled critical volume fraction	Scaled critical volume fraction
Standard positive plate	0.0%	0.0%	N/A	0.0%	60.0%	48.0%
Standard negative plate	0.0%	0.0%	N/A	0.0%	60.0%	58.0%
Porous S38 (Pos)	15.2%	6.1%	4	9.2%	57.2%	45.7%
600 HT (Pos)	11.6%	5.3%	4	6.9%	57.9%	46.3%
600 HT (Pos)	36.9%	19.3%	4	23.7%	51.8%	41.5%
600 HT (Pos)	43.9%	26.2%	4	30.6%	48.0%	38.4%
Skinned SRNL (Pos)	35.4%	17.8%	4	22.2%	52.9%	42.3%
K25 HGMs (Pos)	13.2%	6.1%	4	7.9%	57.5%	46.0%

$$R = \frac{CS}{t} \times (p\%) \quad (13)$$

where R is the discharge rate in $A\ g^{-1}$, CS is the specific stoichiometric capacity of the positive active material, t is the time of discharge in hours, and $p\%$ is the expected utilization at the discharge rate. It was estimated that a plate discharged at the 1 h or 1C rate would have about 30%, the 2C rate would have 25%, and the 4C rate would have 20% utilization of the positive active material. The discharge rates that were used for our tests were $0.067\ A\ g^{-1}$ for the 1C rate, $0.112\ A\ g^{-1}$ for the 2C rate and $0.179\ A\ g^{-1}$ for the 4C rate. While these rates were programmed into the test equipment to approximate the 1C–4C rate, the actual $A\ g^{-1}$ rate that occurred for the discharge is what's reported and used for the modeling.

In Fig. 13, the utilization of the positive active material relative to its stoichiometric capacity is plotted for all the plates tested having PHGM additives. The plates with the porous S38 additives provided the best experimental results. Most of the PHGM plates performed better than the Standard Plates over the entire range of discharge rates tested, although at the highest discharge rates, all the plates appeared similar. At the highest discharge rates, small changes in the external resistance of the cell can result in large voltage drops and cause variations in the performance of the cell independent of the plate parameters. These types of limiting factors can restrict the performance of a lead acid battery at discharge rates greater than the 2C–4C discharge rate (~ 0.11 – $0.20\ A\ g^{-1}$). Because the utilization is better for all high discharge rates, adding PHGM's to a positive plate would provide better performance for many applications, but the benefits would depend on the cell design. The maximum benefit would occur when a cell is designed specifically with these additives.

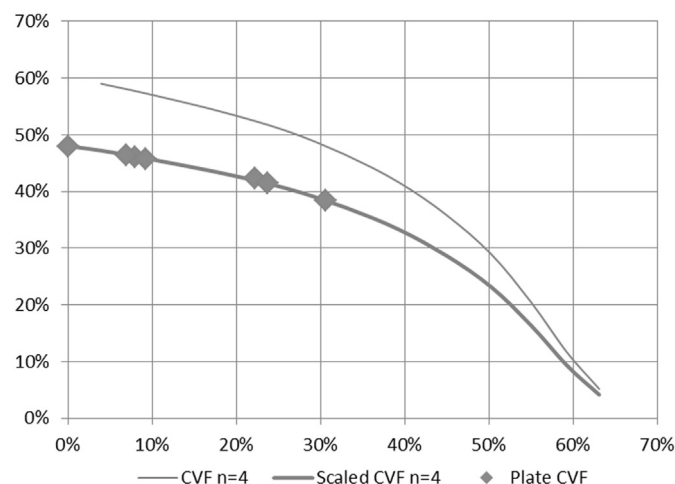


Fig. 11. Scaled and un-scaled critical volume fractions (CVF) for $n = 4$ particles used for modeling non-conductive additive plates.

The skinned PHGMs at a loading of 35.4%, the Porous S38s (PS38s) etched at a loading of 15.2%, and the SRNL 600 HT PHGMs at loadings of 11.6%, 36.9% and 43.9% are all plotted in Fig. 13 along with the hand pasted standard plate. Only the 35.4% skinned PHGM plates performed worse than the standard plate. These plates were reprocessed PHGMs and performed better than the Standard Plates at the low rate but did not perform as well at the high rates. Baseline tests were performed on commercial and hand pasted standard plates as shown in Fig. 14. The hand pasted standard plate did not perform as well as the commercial plate particularly at the lower 1C discharge rate ($0.067\ A\ g^{-1}$).

All the standard and PHGM plates were modeled and compared to the experimental data in order to evaluate some of the possible problems that the PHGM plates may have exhibited. The porosity experimental data showed that the PHGMs did at least partially fill with water during pasting. After soaking the cured plates in water, the PHGMs were completely filled indicating that these additives functioned as expected. Although the result that the PHGMs were filled after being soaked is encouraging, we did find that many of the PHGM plates did not perform as well as expected compared to the model. We believe that the diffusion of the ions through the walls of the PHGMs or the difficulty in forming plates with the PHGMs might be limiting the performance of these plates. The model is used to investigate these problems by comparing models which include these effects to the experimental data provided in Figs. 15–19 to gain more insight into the plate's performance.

For convenience, Table 6 shows the unique parameters for each type of plate tested including active material mass, active material porosity, critical volume fraction, initial acid concentration, and external resistance. The total plate porosity and the CVF are provided in Tables 4 and 5, respectively. The model parameters for the initial acid concentration and external resistance were estimated from the discharge voltage curves. Initial concentration affects the initial voltage and is independent of the currents. External resistance affects the initial voltage drop in proportion with the current applied.

In Figs. 15–19, the blue line (in the web version) having circles is the discharge data from the best observed plate at each current tested. The solid red line (in the web version) represents the model prediction of the plate's performance. The figures showing the PHGM plates also have two additional curves. One of the curves is the model for the plate where the active material has been discharged by 15% before simulating the discharge. This model investigates the possibility that the formation was only 85% complete (or 15% discharged). The result of this discharge model is shown on the figures with a dashed red line (in the web version). We also used the model to investigate the possibility that the porous additives did not perform as well as expected. For instance a sphere that fills with electrolyte but does not allow sufficient diffusion through the PHGMs walls during discharge will look more like a non-porous additive (i.e. HGM additive) than a porous one. To

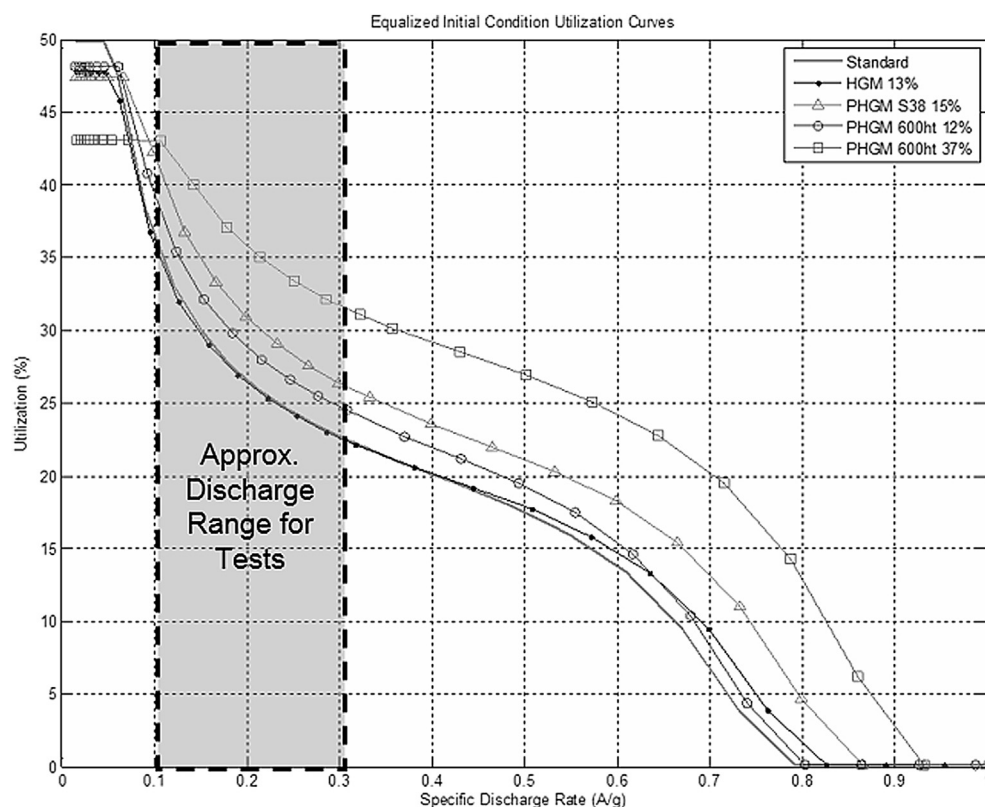


Fig. 12. Utilization curves based on model and specific discharge rate. The dashed lines mark the approximate discharge range of the tests performed.

explore the limiting case of completely non-porous additives, we have reduced the PHGM plate porosity in the model to the amount that would have been present if the internal volume of the PHGMs was not present. The result of this discharge model is shown on the figures with a dot-dashed black line (in the web version).

The discharge data for the best performing hand pasted standard plate is shown in Fig. 15. Comparing the data with the model (solid red line (in the web version)), we see good performance comparison for the 2C, 4C, and 10 A discharge curves. The performance deviation on the 1C rate may be attributed to incomplete

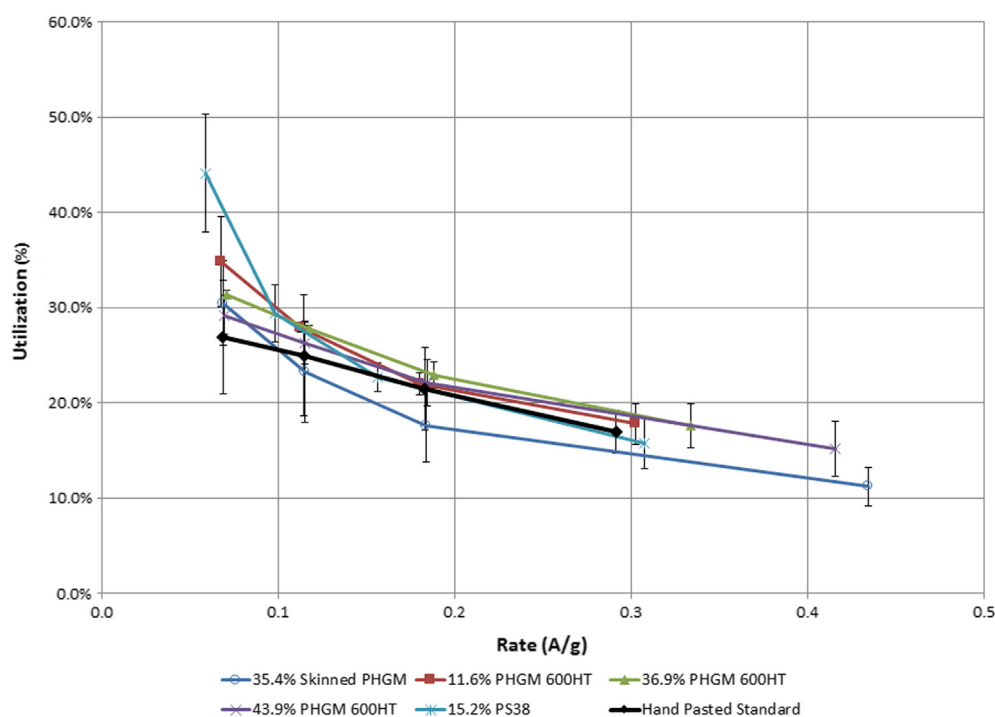


Fig. 13. Average utilizations vs. discharge rate ($A g^{-1}$) for variable rate cycling with standard deviations.

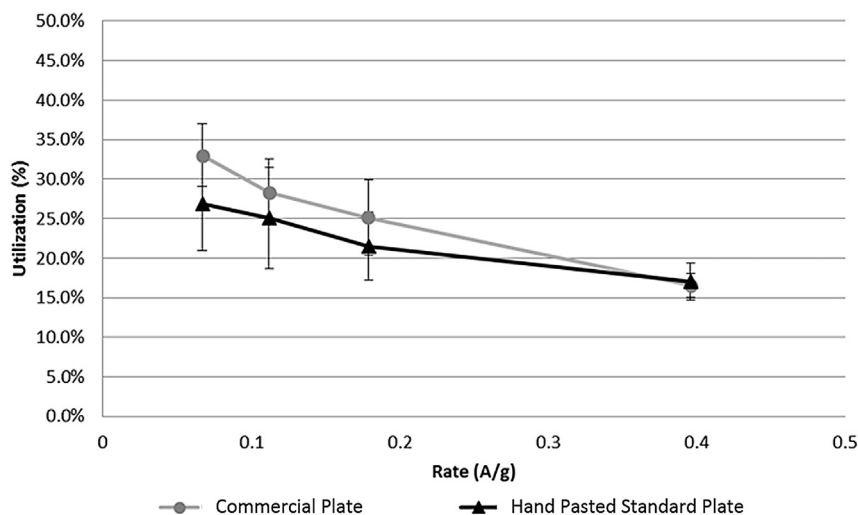


Fig. 14. Utilizations vs. discharge rate comparisons of commercial and hand pasted positive standard plates.

formation. In all of the tests, the 1C rate was the first set of discharges performed after formation and conditioning cycles were completed. We believe the formation may have been incomplete on this set of discharges. The data did compare close to the 15% unformed model curve (dashed red line (in the web version)). As this was the standard hand pasted plates, and there were no additives in this plate, there is no additive model to show. The model results are more consistent with discharge results for the commercial plates; see Fig. 14, than the hand pasted standard plates.

The discharge data and associated models of a battery plate that contained 15.2% of the PS38 PHGMs are shown in Fig. 16. The data falls short of the model (solid red lines (in the web version)) for all discharge rates. The data also falls below the non-porous additive model (dot-dashed black lines). This plate's discharge curves are better than the 15% unformed model (dashed red lines (in the web version)). We believe that the performance degradation is most

likely due to incomplete formation. However, the possibility that the ions are having difficulties in diffusing through the PHGM porous walls cannot be eliminated.

For all the plates with high loadings of PHGMs, we believe that incomplete formation is the reason for the lack of performance. The plates with a high loading of PHGMs include the processed SRNL PHGMs, 35.4%. The discharge curves for those plates are shown in Fig. 17. As previously noted, these spheres had what appeared to be a non-porous skin on their outer surface. This skin was removed using a similar process for creating porous spheres. All these plates performed poorly when compared to the corresponding model for the plate. The other plates having high loadings of PHGMs were the 600 HT SRNL PHGMs with loadings of 43.9% whose discharge curves are shown in Fig. 19. Again, the exact mechanism for this poor performance is not known but we believe the large amount of non-conductive additives make all these plates hard to form.

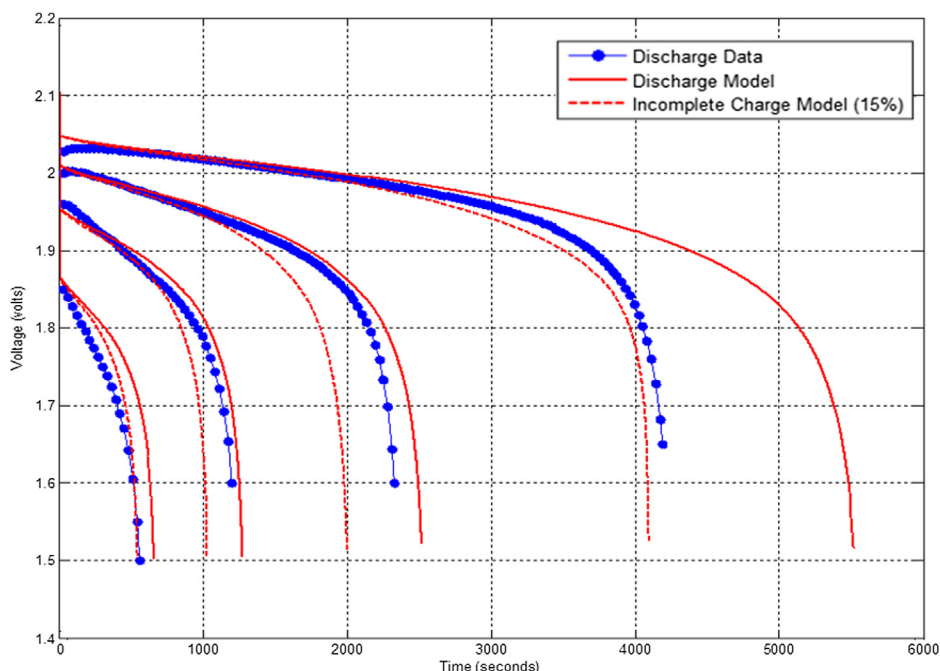


Fig. 15. Discharge data and corresponding discharge models for the best performing hand pasted standard plate.

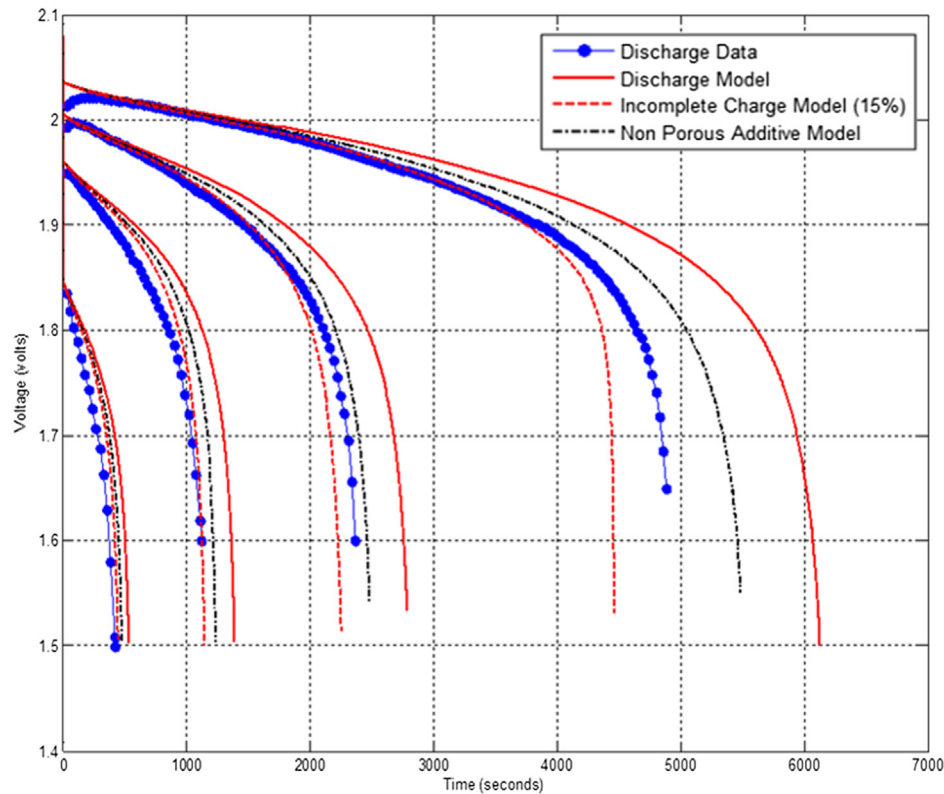


Fig. 16. Discharge data and corresponding discharge models for the best performing 15.2% porous hollow glass microspheres (PHGM) plates.

The plates that performed closest to the model were SRNL's second generation PHGMs that had a relatively low loading of PHGMs, 11.6%. The experimental curves show that the plates performed better than the non-porous additive model curves, see Fig. 18, and demonstrate that the PHGMs were functioning

properly. Also, the experimental curves were essentially identical to the corresponding model's curves at the 2C, 4C, and 10 A discharge rates. The experimental data is only slightly lower than the model at the 1C rate which can be attributed to some incomplete formation for the initial plate tests that occur at the 1C rate.

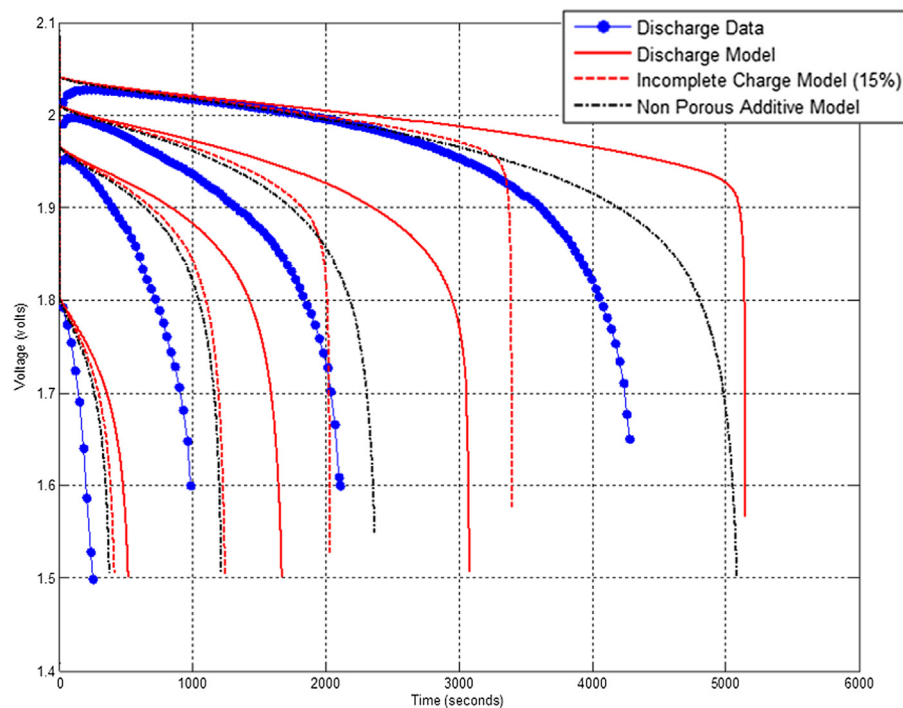


Fig. 17. Discharge data and corresponding discharge models for the best performing 35.4% porous hollow glass microspheres (PHGM) plates.

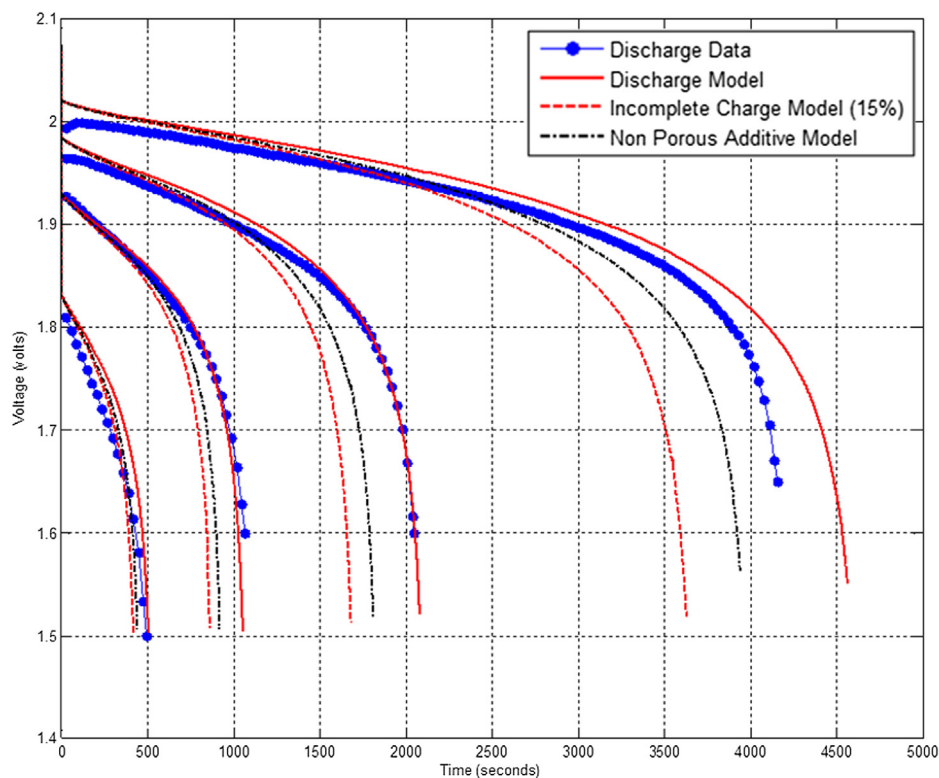


Fig. 18. Discharge data and corresponding discharge models for the best performing 11.6% porous hollow glass microspheres (PHGM) plates.

4. Summary and conclusion

In this paper, we investigated the use of porous, hollow, glass microspheres (PHGMs) in battery paste to increase the porosity of positive electrodes in lead acid batteries. The PHGM additives did

improve electrolyte storage and porosity in the electrodes and improved the specific capacity of the active material. We also developed empirical equations to relate the critical volume fraction, CVF, and porosity of an electrode to the amount, size, and porosity of the additives in that electrode. The porosity estimates made from

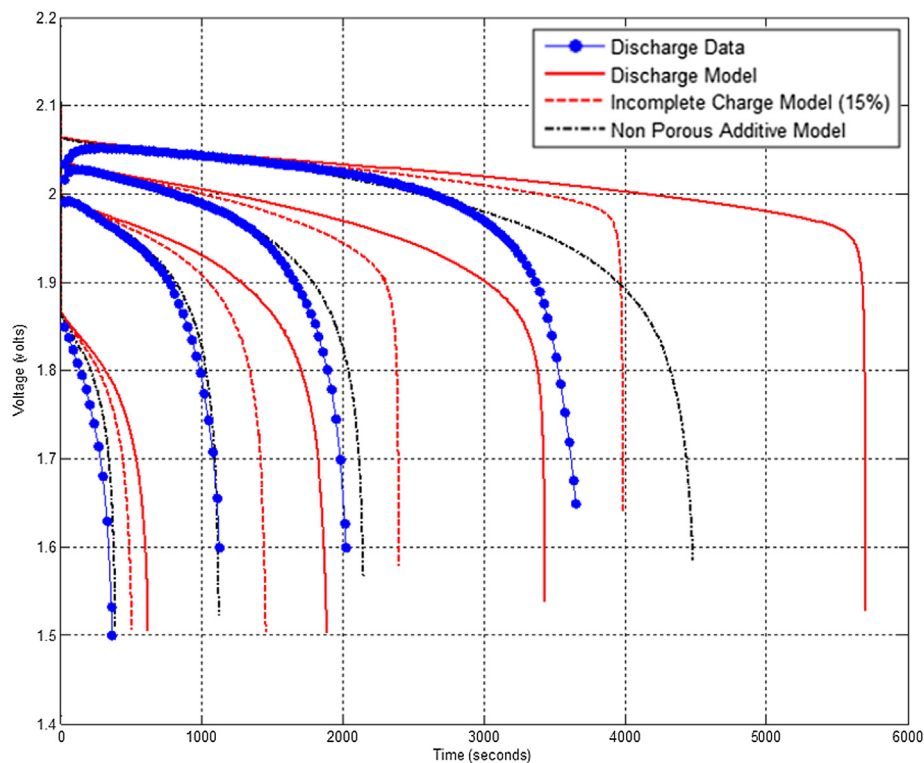


Fig. 19. Discharge data and corresponding discharge models for the best performing 43.9% porous hollow glass microspheres (PHGM) plates.

Table 6

Parameters for plates whose discharged voltage vs. time plots are shown in Figs. 15–19.

Plate type	Active material mass (g)	Active material porosity (%)	Critical volume fraction (%)	Initial acid concentration (mol L ⁻¹)	External resistance (mΩ)
Hand pasted standard	34.00	51.90%	50.00%	5.1	16
UI porous S38 additives 15.2%	32.25	55.10%	47.60%	4.1	16
SRNL (processed) PHGM additives 35.4%	22.8	59.20%	44.10%	4.3	21
SRNL 600 HT PHGM additives 11.6%	32.7	53.5%	48.3%	3.9	17
SRNL 600 HT PHGM additives 43.9%	29.71	57.50%	40.00%	5.1	16

the empirical equations compare favorably with the experimental data from plates fabricated with these additives. Because the nonconductive PHGMs do reduce the critical volume fraction (CVF) of the electrodes as predicted from conductivity models, the increase in electrode performance due to increased porosity was partially offset by the drop in capacity due to a lower CVF. The performance of electrodes with additives is estimated from computer models using the electrode's CVF and porosity as provided by the equations.

Tests were performed on plates having volume loadings of PHGMs from 11% to 44% of total solids in positive electrodes to determine their effect on the active material utilizations at high rates. The results from these discharge tests were reported and compared with theoretical models with good success. Although all of the PHGM plates except one (i.e. the skinned PHGMs) performed better than the standard baseline plate, only the plates with low loadings of PHGMs performed as expected by our models. The plate providing the closest comparison to our models had low loadings, 11.6%, of SRNL's second generation PHGMs and these plates demonstrated that adequate diffusion of ions through the PHGMs occurred and that the plates were formed.

In conclusion, the PHGMs could provide improved performance for lead acid batteries. The major problem with these plates occurred at high loadings of PHGMs which caused difficulty in the formation process and appeared to disrupt the conductive network of the active material. At lower loadings of PHGMs, the plates performed as expected and the diffusion of ions through the PHGM walls was adequate. Although the PHGMs did provide benefits to the plates tested, these were very thin (i.e. ~0.050 in. or ~0.127 cm) positive plates and the cell had an excess of electrolyte. Thicker, long-life plates and specially designed cells would realize the most benefit from the use of PHGMs in the active material. Fabricating conductive coatings on the outer layer of the PHGMs could significantly improve the performance of the PHGM plates as the conductive PHGMs would not significantly reduce the CVF of the active material. An additive having the attributes of increasing the amount of stored electrolyte and porosity in plates while simultaneously improving the overall conductive network of the plate would be ideal for many applications.

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References

- [1] H. Bode, Lead-Acid Batteries, John Wiley & Sons, New York, 1977.
- [2] P.T. Moseley, J. Power Sources 64 (1997) 47–50.
- [3] F. Cheng, J. Liang, Z. Tao, J. Chen, Adv. Mater. 23 (2011) 1695–1715.
- [4] D. Berndt, Maintenance-Free Batteries, John Wiley & Sons, New York, 1997.
- [5] H. Metzendorf, J. Power Sources 7 (1982) 281–291.
- [6] K.-J. Euler, R. Kirchhof, H. Metzendorf, J. Power Sources 5 (1980) 255–262.
- [7] T. Woodland, M. Sorge, S. Zhang, T. Bean, S. McAllister, J.R. Canning, Y. Xie, D.B. Edwards, J. Power Sources 230 (2013) 15–24.
- [8] D.B. Edwards, V. Srikanth, J. Power Sources 34 (1991) 217–232.
- [9] D.B. Edwards, P. Appel, B. Hammond, J. Power Sources 38 (1992) 287–294.
- [10] Leung K. Heung, Ray F. Schumacher, George G. Wicks, Hollow Porous-Wall Glass Microspheres for Hydrogen Storage, US 7666807 B2.
- [11] Ray F. Schumacher, Apparatus and Process to Enhance the Uniform Formation of Hollow Glass Microspheres, US 8544297 B2.
- [12] G.G. Wicks, L.K. Heung, R.F. Schumacher, Am. Ceram. Soc. Bull. 87 (2008) 23–28.
- [13] Y. Xie, S. McAllister, D.B. Edwards, I.F. Cheng, J. Power Sources 196 (2011) 10727–10730.
- [14] J. Newell, S. Patandar, D.B. Edwards, J. Power Sources 188 (2009) 292–295.
- [15] M. Fuji, C. Takai, R.V. Rivera Virtudazo, Adv. Powder Technol. 25 (2014) 91–100.
- [16] R.V.R. Virtudazo, M. Fuji, T. Shirai, Mater. Lett. 65 (2011) 3112–3115.
- [17] L. Lam, O. Lim, H. Ozgun, D.A.J. Rand, J. Power Sources 48 (1994) 83–111.
- [18] B. Hariprakash, A.U. Mane, S.K. Martha, S.A. Gaffoor, S.A. Shivashankar, A.K. Shukla, J. Appl. Electrochem. 34 (2004) 1039–1044.
- [19] K. Sawai, T. Funato, M. Watanabe, H. Wada, K. Nakamura, M. Shiomi, S. Osumi, J. Power Sources 158 (2006) 1084–1090.
- [20] R. Ponraj, S. McAllister, I. Francis Chenga, D.B. Edwards, J. Power Sources 189 (2009) 1199–1203.
- [21] S. Patandar, S. McAllister, I. Cheng, D.B. Edwards, J. Power Sources 195 (2010) 362–366.
- [22] S. McAllister, S. Patandar, I. Cheng, D.B. Edwards, Scr. Mater. 61 (2009) 375–378.
- [23] Y. Chen, Q. Ni, W. Han, D.W. Kirk, S.J. Thorpe, Scr. Mater. 65 (2011) 986–989.
- [24] D.B. Edwards, P. Appel, J. Power Sources 38 (1992) 281–286.
- [25] S. Zhang, D.B. Edwards, J. Power Sources 158 (2006) 927–931.
- [26] D.B. Edwards, S. Zhang, J. Power Sources 172 (2007) 957–996.
- [27] S. Zhang, T. Bean, D.B. Edwards, J. Power Sources 195 (2010) 883–889.
- [28] P. Appel, D.B. Edwards, Adv. Perform. Mater. (APM) (3.1) (1996).
- [29] R. Cantrell, D.B. Edwards, P. Gill, J. Power Sources 73/2 (1998) 204–216.
- [30] R. Harwood, V.S. Manoranjan, D.B. Edwards, IEEE Transactions on Energy Conversion TEC-00504-2010.R1.
- [31] A.V. Kyrylyuk, A. Wouterse, A.P. Philipse, Prog. Colloid Polym. Sci. 137 (2010) 29–33.

Glossary

CVF: critical volume fraction
 N: total quantity of nodes in the conductivity model
 N_A: quantity of nodes replaced by additives in the conductivity model
 N_A/N: fraction of nodes replaced by additives in the conductivity model
 f_S: fraction of solid volume occupied by additives in the battery paste
 f_T: fraction of total volume occupied by additives in the battery paste
 Z: porous fraction of PHGM
 n: ratio of additive size to node size (diameters)
 HGM: hollow glass microsphere
 PHGM: porous hollow glass microsphere
 p%: expected utilization at discharge rate
 t: time of discharge in hours
 R: discharge rate (amp g⁻¹)
 CS: stoichiometric capacity
 IC: one hour discharge rate
 V_T: total volume of plate
 V_P: volume of porosity in plate
 V_{AD}: volume of additive in plate
 V_{AM}: volume of active material in plate
 ΔV_P: reduction in porosity due to additives
 P_A: porosity of plate not including internal volume of PHGMs
 P_S: porosity of standard plate having no additives
 P: total porosity of the plate